## GCE MARKING SCHEME

CHEMISTRY AS/Advanced

## SUMMER 2012

## CH5

## SECTION A

1. (a) $1 \mathrm{dm}^{3}$ at $20^{\circ} \mathrm{C}$ contains 52.9 g and at $0^{\circ} \mathrm{C}$ it contains 17.5 g
$\therefore$ amount crystallised $=52.9-17.5=35.4 \mathrm{~g}$ (1)
(b) (i) 2 mol of $\mathrm{K}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ give 1 mol of $\mathrm{O}_{2}$

2 mol of $\mathrm{K}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ give $29.0 \mathrm{dm}^{3}$ of $\mathrm{O}_{2} \quad$ (1)
$\therefore \quad 0.1 \mathrm{~mol}$ of $\mathrm{K}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ gives $29.0 / 20=1.45 \mathrm{dm}^{3}$ of oxygen (1)
(ii) Measure the volume of oxygen produced at specified time intervals /

Measure the pH of the solution at specified time intervals
(c) (i) An (inert) electrode that is used to carry the charge / current / electron flow
(ii) A comment on the relative values (e.g. the persulfate system is the more positive of the two systems)
(1)

The more positive 'reagent' / persulfate ions acts as the oxidising agent, accepting electrons via the external circuit (1)

- must have the first mark to get second
(d) (i) The experiments show that both the concentrations of iodide and persulfate have doubled (1) therefore the initial rate should increase four times

$$
4 \times 8.64 \times 10^{-6}=3.46 \times 10^{-5}
$$

(ii) Rate $=\mathrm{k}\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]\left[\mathrm{I}^{-}\right]$

$$
\begin{align*}
\therefore \mathrm{k} & =\frac{8.64 \times 10^{-6}}{0.0400 \times 0.0100}  \tag{1}\\
& =0.0216(1) \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \tag{1}
\end{align*}
$$

(iii) In the rate equation one $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ ion reacts with one $\mathrm{I}^{-}$ion.

The rate-determining step therefore has to have 1 mole of each reacting, as (only) seen in step 1
(1) for correct sign (1) for correct number
(b) (i) hydration $\qquad$ lattice breaking
(ii) e.g. add a small 'amount' of an alkali / sodium hydroxide / $\mathrm{NaOH} / \mathrm{OH}^{-}$ions (1) this would remove / react with hydrogen ions giving water, shifting the position of equilibrium to the left (removing iodine) add $\mathrm{Pb}^{2+} / \mathrm{Ag}^{+}$ect.
(c) (i) Any TWO from
white / misty fumes (of HI)
yellow solid / solution (of sulfur)
brown / black solid / purple vapour (of iodine)
bubbles / effervescence / fizzing
One mark for each correct response
(ii) The values show that chlorine is the best oxidising agent, as it has the most positive $\mathrm{E}^{\theta}$ value and therefore iodide is the better reducing agent (1) and is 'strong' enough to reduce the sulfuric acid. / OWTTE (1)
(d) (i) $2 \mathrm{NaOH}+\mathrm{Cl}_{2} \rightarrow \mathrm{NaOCl}+\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$
(ii) e.g. bleach, kills bacteria
3. (a) (i)

$$
\text { Number of moles of EDTA }=\frac{19.20 \times 0.010}{1000}=1.92 \times 10^{-4} / 0.000192
$$

- error carried forward throughout (a)
(ii) $1.92 \times 10^{-4} / 0.000192$
(iii) Concentration $=\frac{1.92 \times 10^{-4} \times 1000}{50}=3.84 \times 10^{-3} / 0.00384 \mathrm{~mol} \mathrm{dm}^{-3}$

$$
\begin{equation*}
\text { Concentration }=3.84 \times 10^{-3} \times 63.5=0.244 \mathrm{~g} \mathrm{dm}^{-3} \tag{1}
\end{equation*}
$$

(iv) $\% \mathrm{Cu}=\frac{0.244 \times 100}{11.56}=2.11$
(b) Transition elements have either a partly filled 3d sub-shell or form ions that have a partly filled 3 d sub-shell
However copper forms $\mathrm{Cu}^{2+}$ ions that are ' $3 \mathrm{~d}^{9}$ ' / partly filled 3 d sub-shell (1)
whereas $\mathrm{Zn}^{2+}$ ions are ' $3 \mathrm{~d}^{10}$, / full 3 d sub-shell (1) - any 2 from 3
QWC Organisation of information clearly and coherently; use of specialist vocabulary where appropriate.
(c)

| Complex ion | Shape | Colour |
| :---: | :---: | :---: |
| $\left[\mathrm{CuCl}_{4}\right]^{2-}$ | tetrahedral | yellow / <br> lime green |
| $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ | octahedral | deep blue |

Any two correct (1) all correct (2)
(d) The more negative the $\Delta H_{f}$ value the more stable the oxide (1)

PbO is relatively the more stable / CuO is relatively the less stable (1)
(e) (i) Any TWO from
variable oxidation states
partially filled 3d energy levels
ability to adsorb 'molecules'
ability to form complexes with reacting molecules / temporary / co-ordinate bonds
One mark for each correct response
(ii) e.g. to allow lower pressures / temperatures
use recyclable catalysts - needs qualifying
longer lasting / less toxic catalysts

## SECTION B

4. (a)
$\mathrm{CO} \rightarrow$
C +2
$\mathrm{CO}_{2} \rightarrow+4$
Increase of (positive) oxidation number $=$ oxidation $/$ reducing agents themselves are always oxidised are always oxidised (1)

OR

$$
\begin{equation*}
\mathrm{I}_{2} \mathrm{O}_{5} \rightarrow \mathrm{I}+5 \quad \mathrm{I}_{2} \rightarrow \mathrm{I}_{2} \quad 0 \tag{1}
\end{equation*}
$$

Oxidation number of iodine reduced, reduction occurring, CO reducing agent
(b) $\quad+2$ state becomes mores stable down the group and +4 becomes less stable.
(c) (i) Add (a little) sodium hydroxide solution (1) to each solution. A white precipitate (1) of aluminium / lead(II) hydroxide (1) is seen. When more sodium hydroxide solution is added these precipitates (dissolve giving a colourless solution). (1)

QWC Legibility of text: accuracy of spelling, punctuation and grammar; clarity of meaning.
(ii) Yellow precipitate (1) $\mathrm{Pb}^{2+}+2 \mathrm{I}^{-} \rightarrow \mathrm{PbI}_{2}$
(d) (i) The bonding of aluminium in the monomer has not completed the octet / suitable diagram / 6 electrons in its outer shell (1) When the dimer is formed this octet of bonded electrons is formed

(ii) (As a catalyst) in the chlorination of benzene / making ionic liquids
(iii) I The number of (gaseous) species is increasing, leading to less order

II For the reaction to be just spontaneous $\Delta \mathrm{G}=0$
substituting $0=60000-88 \mathrm{~T}$

$$
\begin{equation*}
\mathrm{T}=60000 / 88=682 \mathrm{~K} / 409^{\circ} \mathrm{C} \tag{1}
\end{equation*}
$$

 $\left[\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}(\mathrm{aq})\right]$

$$
\begin{array}{ll}
\therefore & 1.26 \times 10^{-5}=\left[\mathrm{H}^{+}\right]^{2} / 0.10 \\
\therefore & {\left[\mathrm{H}^{+}\right]^{2}=1.26 \times 10^{-6} \quad[1]} \\
\therefore & {\left[\mathrm{H}^{+}\right]=\sqrt{ } 1.26 \times 10^{-6}=1.12 \times 10^{-3} / 0.00112} \tag{1}
\end{array}
$$

- error carried forward

$$
\begin{equation*}
\mathrm{pH}=-\log _{10}\left[\mathrm{H}^{+}\right]=-\log _{10} 1.12 \times 10^{-3}=2.95 \tag{3}
\end{equation*}
$$

Total [20]
5. (a) (i)

$$
\mathrm{K}_{\mathrm{p}}=\frac{\mathrm{pSO}_{3}(\mathrm{~g}) \times \mathrm{pNO}(\mathrm{~g})}{}
$$

(1) there are no units (1)
(ii) The line for $\mathrm{SO}_{3} / \mathrm{NO}$ at equilibrium should be above the $\mathrm{SO}_{2} / \mathrm{NO}_{2}$ line (1) as $\mathrm{K}_{\mathrm{p}}$ has a value of 2.5, the partial pressures of $\mathrm{SO}_{3}$ and NO at equilibrium will be greater than the partial pressures of $\mathrm{SO}_{2}$ and $\mathrm{NO}_{2}$.
(1)

- accept answer in terms of alternative calculated $\mathrm{K}_{\mathrm{p}}$ value
The line for equilibrium should start at 9 hours. (1) as at equilibrium the concentrations is unchanged as time progresses. (1)

There may be other acceptable forms of explanation to be discussed at the conference
(iii) If the temperature rises then the position of equilibrium will move to the left, (reducing the quantities of $\mathrm{SO}_{3}$ and NO ). (1)
This will make the value of $K_{p}$ smaller. (1)
(b) (i) Nitric acid is a strong acid and its pH is low / $<2 / 1.0$ (1)

As aqueous ammonia is added the pH slowly rises (1) until a pH of $\sim 3$ is reached, when it rises rapidly
At a pH of 8-9, it tails off slowly as ammonia is a weak base. (1)
Accept any 3 from 4
Selection of a form and style of writing which is appropriate to purpose and to complexity of subject matter
(ii) The equivalence point is reached when $20.0 \mathrm{~cm}^{3}$ of ammonia solution has been added as this is at the mid point of the more vertical section. (1)

Since both reagents have the same concentration and the volumes used are both $20 \mathrm{~cm}^{3}$ / the same, the number of moles of each are the same (1)

OR the number of moles of both nitric acid and aqueous ammonia are calculated (0.0020) and shown to be the same (1)

$$
\therefore \text { Mole ratio must be } 1: 1 \text { (1) }
$$

(iii) I Ammonium nitrate is the salt of a strong acid and weak base / there is a buffering effect in operation.
II $\sim 5.5$
(iv) Blue, as bromophenol blue is blue at a pH of 4.7 and above
(c) Number of moles of ammonium nitrate $=\frac{40}{80}=0.50$

- error carried forward

Concentration of ammonium nitrate solution $=\frac{0.5 \times 1000}{200}=2.5 \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore$ Temperature drop $=2.5 \times 6.2=15.5^{\circ} \mathrm{C}$ (1)

